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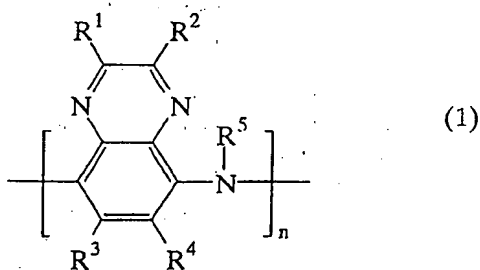
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(54) **Poly(5-aminoquinoxalines); preparation and use thereof.**

(57) Poly(5-aminoquinoxalines) having the general formula (1):



In which R¹ and R² each independently represent a hydrogen atom, a hydroxyl group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a thienyl group, a substituted thienyl group, a naphthyl group, a substituted naphthyl group, a pyrrolyl group, a substituted pyrrolyl group, a furyl group,

a substituted furyl group, an alkyl group, an alkoxy group, or an alkoxy group; R³ and R⁴ each independently represent a hydrogen atom, an alkyl group, an alkoxy group, a cyano group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a thienyl group, a substituted thienyl group, a pyrrolyl group, a substituted pyrrolyl group, a furyl group, a substituted furyl group, a naphthyl group, or a substituted naphthyl group; R⁵ represents a hydrogen atom, an alkyl group, an alkoxy group, an acetyl group, a cyano group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a thienyl group, a substituted thienyl group, a pyrrolyl group, a substituted pyrrolyl group, a naphthyl group, or a substituted naphthyl group; and n is a positive integer of not less than three. The polymers have excellent thermal resistance, permit easy control of the electrochemical oxidation-reduction potential thereof, have a very narrow band gap of themselves, and have strong fluorescence characteristics.

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Description

BACKGROUND

[0001] The present invention relates to poly(5-aminoquinoxalines), and to preparation and application of the same. Preferred properties of embodiments include excellent thermal resistance, easy control of electrochemical oxidation-reduction potential, a very narrow band gap and strong fluorescence characteristics.

[0002] These polymers have an electron-donating group and an electron-accepting group in one molecule thereof, whereby they have p-type and n-type semiconductor characteristics. These compounds can easily be formed into a thin film by the spin coating method, and can be applied as an active substance or an electrode material for a battery, an organic electroluminescence device material, an electroluminescence device material, a semiconductor, a semiconductor device, and a nonlinear-type optical material.

[0003] In recent years, aromatic compounds with a π conjugated system spread in two dimensions and heterocyclic compounds having a hetero-atom have been used for a variety of electronic devices through utilization of their light emission characteristics and electron and positive hole transport characteristics. For example, organic electroluminescence devices are generally classified into high polymeric devices utilizing the π conjugated system and low molecular weight devices with various functions separately possessed by layers which are laminated. Particularly, in the case of the low molecular weight materials, there has been a requirement for their carrier mobility and fluorescence characteristics, and it has been required to freely change the band gap in developing derivatives thereof. In addition, for these materials, film characteristics thereof are important, and they have been demanded particularly to form a stable amorphous film (Polymer, 24(1983), p. 748; Jpn. J. Appl. Phys. 25(1986), L773; Appl. Phys. Lett. 51(1987), P. 913; USP No. 4,356,429).

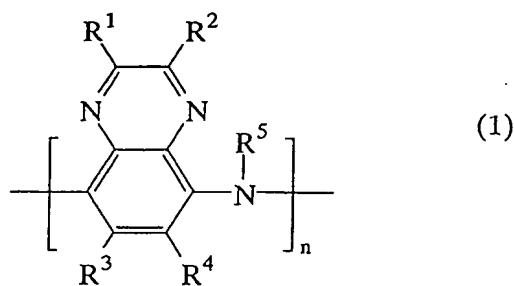
[0004] In the battery field there is a demand for control of the oxidation and reduction potentials of the compound (for example, Denki Kagaku Oyobi Kogyo Butsuri Kagaku (Electrochemistry and Industrial Physical Chemistry); Vol. 54, p. 306 (1986)). As to the electrode active substance used in the battery, in relation to the electrolyte, it is necessary to set the oxidation-reduction potential of the substance to within the dissociation voltage of the electrolyte, and, therefore, control of the oxidation-reduction potential has been an important problem.

[0005] As for the semiconductor characteristics, π conjugated system polymers have been investigated for the purpose of achieving a narrower band gap, but, generally, the π conjugated system polymers are insoluble in solvents and are difficult to deal with, and it has been difficult to control the structure of the polymers. In addition, as another method of narrowing the band gap, there is a method of spreading the π conjugated system in two dimensions (Synthetic Metals, 69(1995), pp. 599-600; J. Am. Chem. Soc. 117(25), 1995, pp. 6791-6792), but these materials are also insoluble and infusible and are inconvenient to deal with. Besides, general π conjugates system polymers can display behaviors as an impurity semiconductor upon being doped with an impurity, but it has been difficult to stably form p-type and n-type semiconductors from one substance.

[0006] The present invention has been completed based on the results of earnest studies in search of a compound having a novel molecular structure, in consideration of the above circumstances. Accordingly, it is an object of the present invention to provide new and useful poly(5-aminoquinoxalines). Particular embodiments may have any one or more of the following properties, namely that they have excellent thermal resistance, are soluble in water or an organic solvent, permit control of degree of depolarization and electrochemical oxidation-reduction potential thereof, show a clear color change due to chemical or electrochemical oxidation or reduction, and are themselves electrically conductive.

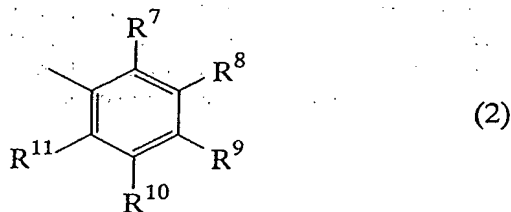
[0007] Further aspects of the present invention utilize such novel poly(5-aminoquinoxalines) as an organic electroluminescence device, an electrochromic device, an active substance or an electrode for a battery, a semiconductor, an n-type semiconductor, a solar-cell electrode, a non-linear device, etc., preferably forming the novel poly(5-aminoquinoxalines) into a film or the like through the spin coating method or the like.

[0008] In accordance with one aspect of the present invention, there is provided a poly(5-aminoquinoxaline) having the general formula (1):



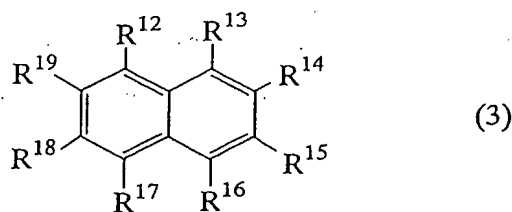
15 in which R^1 and R^2 each independently represent a hydrogen atom, a hydroxyl group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a thienyl group, a substituted thienyl group, a naphthyl group, a substituted naphthyl group, a pyrrolyl group, a substituted pyrrolyl group, a furyl group, a substituted furyl group, an alkyl group, or an alkoxy group; R^3 and R^4 each independently represent a hydrogen atom, an alkyl group, an alkoxy group, a cyano group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a thienyl group, a substituted thienyl group, a pyrrolyl group, a substituted pyrrolyl group, a furyl group, a substituted furyl group, a naphthyl group, or a substituted naphthyl group; R^5 represents a hydrogen atom, an alkyl group, an alkoxy group, an acetyl group, a thienyl group, a substituted thienyl group, a pyrrolyl group, a substituted pyrrolyl group, a naphthyl group, or a substituted naphthyl group; and n represents a positive integer of not less than three. R^1 and R^2 may be the same. Preferred R^1/R^2 groups are disclosed below; note that the R^1/R^2 combinations may or may not be the same on all repeat units of the polymer although often they are; the same applies to other R group choices, so that a given polymer may embody more than one of the options given below.

25 [0009] In the general formula (1) above, R^1 and R^2 may independently be groups having the general formula (2):



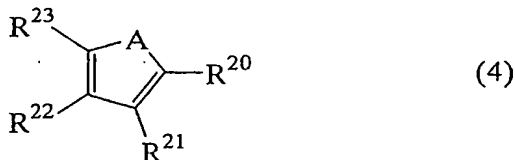
40 in which R^7 to R^{11} each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, a cyanoalkyl group having one to four carbon atoms, a haloalkyl group having one to four carbon atoms, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group.

[0010] In the general formula (1) above, R^1 and R^2 may independently be groups having the general formula (3):



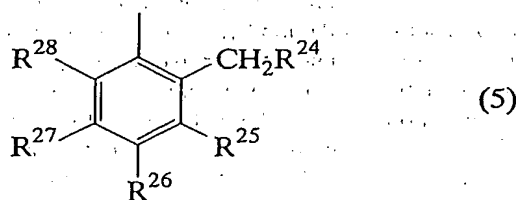
55 in which either one of R^{12} to R^{19} is coupled to the quinoxaline ring; and the others of R^{12} to R^{19} each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group.

[0011] In the general formula (1) above, R^1 and R^2 may independently be groups having the general formula (4):



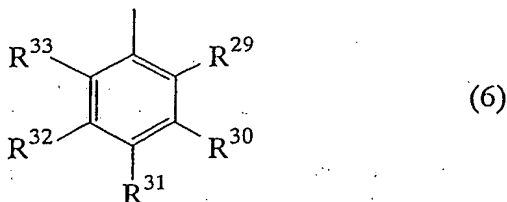
10 in which either one of R^{20} to R^{23} is coupled to the quinoxaline ring; the others of R^{20} to R^{23} each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group; and A represents NH, O, or S.

15 [0012] In the general formula (1) above, R^1 and R^2 may independently be groups having the general formula (5):



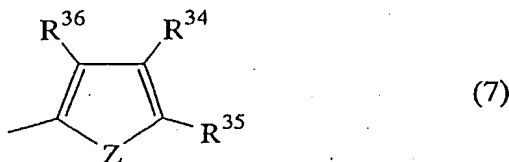
in which R^{24} represents a halogen atom or a cyano group; and R^{25} to R^{28} each independently represent a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group.

30 [0013] In the general formula (1) above, R^5 may be a group having the general formula (6):



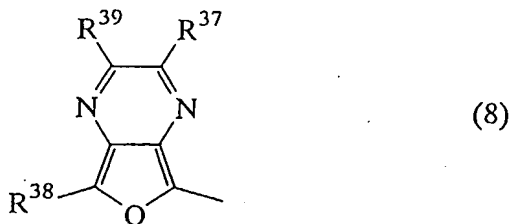
45 in which R^{29} to R^{33} each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group.

[0014] In the general formula (1) above, R^5 may be a group having the general formula (7):



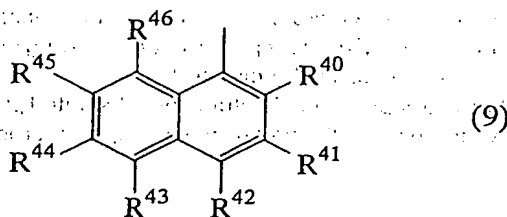
in which R^{34} to R^{36} each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group; and Z represents NH, O, or S.

[0015] In the general formula (1) above, R^5 may be a group having the general formula (8):



in which R^{37} to R^{39} each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group; and Q represents NH, O, or S.

[0016] In the general formula (1) above, R^5 may be a group having the general formula (9):



in which R^{40} to R^{46} each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group.

[0017] In accordance with another aspect of the present invention, there are provided applications of the poly(5-aminoquinoxaline) represented by the general formula (1) above. The applications of the poly(5-aminoquinoxaline) of the general formula (1) reside in: a film formed by spin coating or casting of a poly(5-aminoquinoxaline) of the formula (1); a film formed by compression molding of a poly(5-aminoquinoxaline) of the formula (1); an electrochromic device including a poly(5-aminoquinoxaline) of the formula (1); an active substance or an electrode for a battery, including a poly(5-aminoquinoxaline) of the formula (1); a semiconductor including a poly(5-aminoquinoxaline) of the formula (1); a p-type semiconductor produced by oxidizing a poly(5-aminoquinoxaline) of the formula (1) by an oxidant or electrochemical doping; an n-type semiconductor produced by reducing a poly(5-aminoquinoxaline) of the formula (1) by a reducing agent or electrochemical doping; a solar cell comprising the p- and n-type semiconductors; an organic electroluminescence device including a poly(5-aminoquinoxaline) of the formula (1); and a non-linear organic material including a poly(5-aminoquinoxaline) of the formula (1).

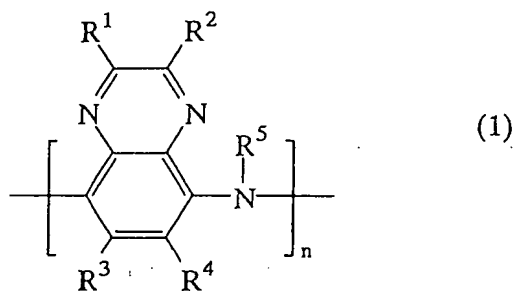
[0018] The novel poly(5-aminoquinoxalines) according to the present invention have good thermal resistance and we find are soluble in water or organic solvents. Therefore, the polymers find a wide range of utilization, and can be dry formed into fibers, films and the like by utilizing solutions obtained by dissolving the polymers in appropriate solvents. In addition, due to the structure thereof, we have found for polymers disclosed herein some excellent properties that are not possessed by the conventional polyarylenes; for example, embodiments of the invention permitted control of the degree of depolarization and the electrochemical oxidation-reduction potential thereof. Besides, according to a method of the present invention which will be described later, it is possible to obtain a polymer in which electric charges are localized along the π conjugated system. In addition, the polymers disclosed herein have been found themselves to be electrically conductive.

[0019] The above and other objects, features and advantages of the present invention will become apparent from

the following description of the embodiments and appended claims of the invention.

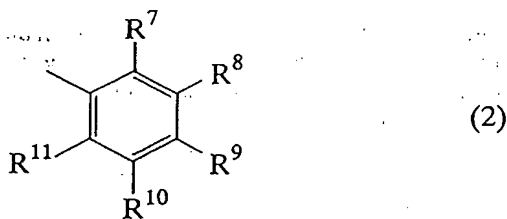
DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0020] The poly(5-aminoquinoxalines) according to the present invention are the polymers represented by the general formula (1):

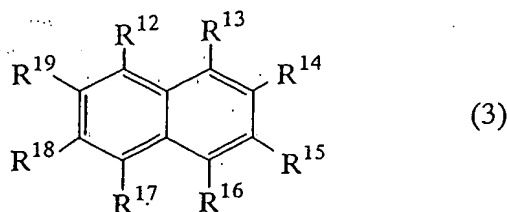


[0021] In the above formula, R¹ and R² each independently represent a hydrogen atom, a hydroxyl group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a thienyl group, a substituted thienyl group, a naphthyl group, a substituted naphthyl group, a pyrrolyl group, a substituted pyrrolyl group, a furyl group, a substituted furyl group, an alkyl group, or an alkoxy group. In this case, the substituent group is preferably an alkyl group or an alkoxy group. The alkyl group or alkoxy group is preferably one having one to ten carbon atoms, particularly one having one to five carbon atoms (the same applies hereinafter).

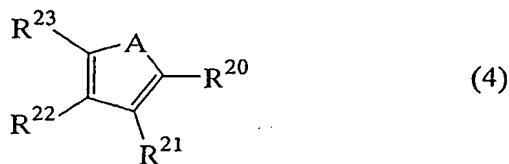
[0022] R¹ and R² are preferably hydroxyl groups, non-substituted or substituted phenyl groups, thienyl groups, naphthyl groups, pyrrolyl groups, or biphenyl groups, and the preferable examples thereof includes the groups represented by the formulas (2) to (5):



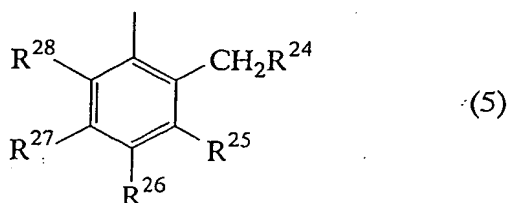
in which R⁷ to R¹¹ each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, a cyanoalkyl group having one to four carbon atoms, a haloalkyl group having one to four carbon atoms, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group;



in which either one of R^{12} to R^{19} is coupled to the quinoxaline ring, and the others of R^{12} to R^{19} each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group;



in which either one of R^{20} to R^{23} is coupled to the quinoxaline ring; the others of R^{20} to R^{23} each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group; and A represents NH, O, or S;



in which R^{24} represents a halogen atom or a cyano group; and R^{25} to R^{28} each independently represent a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group.

[0023] In the general formula (1) above, in consideration of the solubility of the substituent groups R^1 and R^2 , the substituent groups R^1 and R^2 are each desirably a substituted hydroxyl, phenyl, thienyl, naphthyl, pyrrolyl or biphenyl group. In this case, the substituent groups on R^1 and R^2 are each preferably an alkyl or alkoxy group having one to ten carbon atoms, and more preferably an alkyl or alkoxy group having one to five carbon atoms.

[0024] In consideration of amorphousness of a spin-coated film or the like, t-butyl group or t-butoxy group is most suitable. Where R^1 and R^2 are substituted aryl, thienyl or pyrrolyl groups and the substituent groups thereon are each an alkyl group, the compound can further be bromided by use of N-bromosuccinimide, and the bromided compound can further be converted into a cyano compound by reaction with NaCN.

[0025] In the general formula (1) above, R^3 and R^4 each independently represent a hydrogen atom, an alkyl group, an alkoxy group, a cyano group, a hydroxyl group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a thienyl group, a substituted thienyl group, a pyrrolyl group, a substituted pyrrolyl group, a furyl group, a substituted furyl group, a naphthyl group, or a substituted naphthyl group. Among them, a hydrogen atom, an alkyl group and an alkoxy group are preferred.

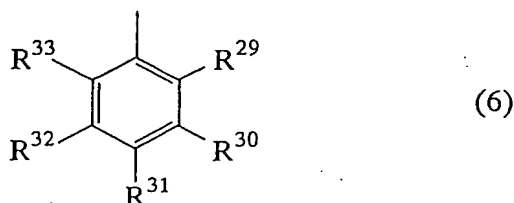
[0026] The alkyl and alkoxy groups used as R^3 and R^4 desirably have one to ten carbon atoms, and more desirably one to five carbon atoms. Further, for enhancing semiconductor characteristics, R^3 and R^4 are each desirably a phenyl, thienyl or naphthyl group or a substituted phenyl, thienyl or naphthyl group. In the case of the substituted groups, the substituent groups are each preferably an alkyl or alkoxy group having one to ten carbon atoms, and more preferably an alkyl or alkoxy group having one to five carbon atoms.

[0027] R^5 in the general formula (1) above represents a hydrogen atom, an alkyl group, an alkoxy group, an acetyl group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, a pyrrolyl group or a substituted pyrrolyl group. Among them, a hydrogen atom, an alkyl group and an alkoxy group are preferred. For stably obtaining an

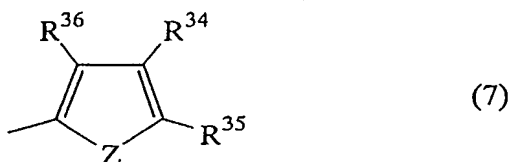
amorphous film of the polymer, R⁵ is preferably at least an alkyl or alkoxy group having one to ten carbon atoms, and more preferably an alkyl or alkoxy group having two to five carbon atoms.

[0028] In addition, for enhancing semiconductor characteristics, R⁵ is preferably a phenyl, naphthyl or thienyl group; in this case, for stably maintaining the amorphousness of the film of the polymer, R⁵ is preferably a substituted phenyl, naphthyl or thienyl group. In the case of the substituted group, the substituent group is preferably an alkyl or alkoxy group having one to ten carbon atoms, and more preferably an alkyl or alkoxy group having one to five carbon atoms.

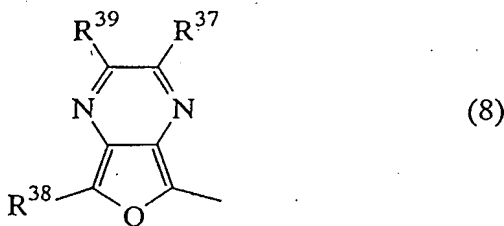
[0029] Examples of R⁵ include the groups represented by the following general formulas (6) to (9):



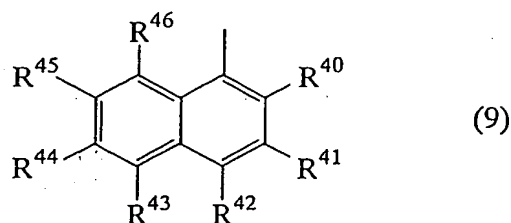
in which R²⁹ to R³³ each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group;



in which R³⁴ to R³⁶ each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group; and Z represents NH, O, or S;



in which R³⁷ to R³⁹ each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group; and Q represents NH, O, or S;

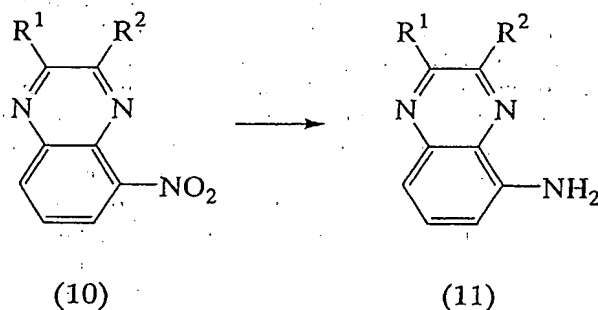


in which R^{40} to R^{46} each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group.

15 **[0030]** Besides, in the general formula (1) above, n is a positive integer of not less than three, and particularly 3 to 400.

[0031] In this case, the molecular weight of the poly(5-aminoquinoxalines) according to the present invention is not particularly limited, but it is preferable that the weight average molecular weight is 1,000 to 100,000, particularly 4,000 to 50,000. Therefore, n in the general formula (1) is preferably such a number as to make the poly(5-aminoquinoxaline) have a weight average molecular weight in the just-mentioned range.

20 **[0032]** In the method of preparing the poly(5-aminoquinoxalines) according to the present invention, 5-aminoquinoxaline constituting a fundamental skeleton in the formula (1) is already known, and can be synthesized by a known method (J. Am. Chem. Soc. 79, pp. 2245-2248 (1957); J. Org. Chem. 31, pp. 3384-3390 (1966)). For example, by dissolving a 5-nitroquinoxaline having the following formula (10) in an appropriate solvent and reducing it by use of Pd/C and hydrogen gas, a 5-aminoquinoxaline of the following formula (11) can be prepared. The 5-nitroquinoxaline of the formula (10) can be synthesized by a known method (J. Chem. Soc., 1953, pp. 2822-2830).



in which R^1 and R^2 have the same meanings as in the general formula (1) above.

45 **[0033]** The method for obtaining the polymer represented by the general formula (1) above is not particularly limited, and there can be used chemical oxidation polymerization, electrolytic oxidation polymerization, and catalytic polymerization. For example, as a general polymerization method, chemical oxidation polymerization is preferably used. In this case, the oxidant is not particularly limited, and ammonium persulfate, tetraammonium peroxide, iron chloride or cerium sulfate are generally used. The polymerization is generally conducted by converting the amine derivative (11), which is the monomer of the polymer represented by the formula (1), into a salt by use of hydrochloric acid, then adding the oxidant, and carrying out the polymerization reaction at a low temperature, preferably at or below 10°C when ammonium persulfate is used, and, in the case where precipitation of the monomer is not observed, more preferably at 0°C. When an oxidation catalyst such as iron chloride or cerium sulfate, the reaction is generally conducted under an atmosphere of N_2 at a reaction temperature of room temperature to 60°C.

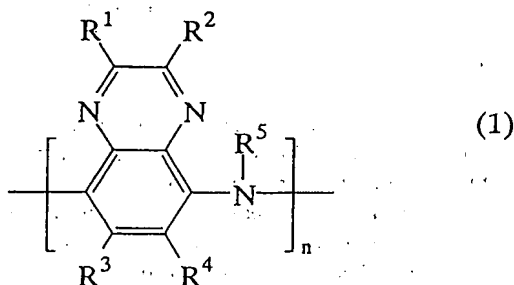
50 **[0034]** As a method for obtaining the polymer from a small amount of the monomer, electrolytic oxidation polymerization is preferably used. The polymerization is generally conducted by converting the amine derivative (11), which is the monomer of the polymer represented by the formula (1), into a salt by use of hydrochloric acid, and then carrying out the oxidation reaction at a low temperature, preferably at or below 10°C, and, in the case where precipitation of the monomer is not observed, more preferably at 0°C. In the polymerization, generally, Ag/Ag^+ is used as a reference electrode, platinum is used as a counter electrode, ITO or platinum electrode is used as a working electrode, and it is

55

important to select the electrodes according to the acidity of the solution. Namely, in the electrolytic oxidation polymerization in a solution with high acidity, preferably platinum electrodes are generally used, while, in a neutral region, ITO, platinum or the like electrodes can be used.

For the electrolytic polymerization, there can be used the potentiostatic electrolysis in which the oxidation potential is measured and then polymerization is conducted potentiostatically while maintaining the potential, the sweep method in which the oxidation potential and the reduction potential are scanned several times, and the galvanostatic electrolysis in which the current is maintained at a constant value; in any case, the polymer can be obtained. In the case of using the monomer (11) which is a precursor of the polymer represented by the formula (1), it is preferable to use the potentiostatic electrolysis at a voltage of 1300 mV, while using Ag/Ag⁺ as the reference electrode, platinum as the counter electrode and ITO as the working electrode, for measuring the oxidation potential.

[0035] Incidentally, where R³ and R⁴ in the general formula (1):



are each a group other than the hydrogen atom, the groups R³ and R⁴ may be introduced into the formula (10) or the formula (11), or may be introduced into the polymer after polymerization. In addition, where R⁵ is a group other than the hydrogen atom, the group R⁵ may be introduced into the formula (11), or may be introduced into the polymer after polymerization. In this case, the introduction of these groups R³, R⁴ and R⁵ can be carried out by a known method.

[0036] The poly(5-aminoquinoxalines) disclosed herein are found generally to be soluble in water and in organic solvents such as dimethylformamide (DMF), N-methylpyrrolidone (NMP), acetonitrile and halogenated benzene, and to be easily formed into a film by the spin coating method or the casting method. In addition we find that powders of the poly(5-aminoquinoxalines) can easily be formed into a film by the compression molding method.

[0037] Compounds disclosed herein, by utilizing the excellent properties thereof, are applicable to films, an electrochromic device, a semiconductor, a battery, a solar cell, an organic electroluminescence device, a non-linear material, and an active substance or an electrode for a battery. In addition, the compounds according to the present invention themselves are electrically conductive. Furthermore, compounds embodying the present invention can be utilized as a p-type or n-type semiconductor, by oxidizing or reducing the compounds through the use of an oxidant or a reducing agent or through electrochemical doping. Incidentally, in forming the compounds of the present invention into films or other formed or molded products, the compounds may be admixed, as required, with compounding ingredients such as heat stabilizer, light stabilizer, filler, reinforcing agent, etc.

EXAMPLE

[0038] Now, the present invention will be described more specifically and in detail below referring to examples thereof, but the invention is not limited to the examples.

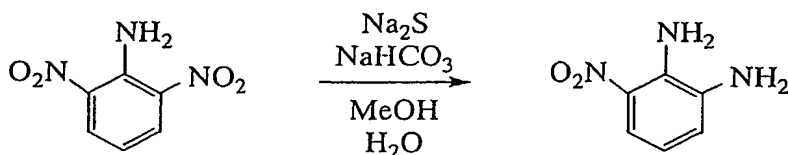
Synthesis Example 1

Synthesis of 2,3-Dihydroxy-5-aminoquinoxaline

[0039] 2,3-Dihydroxy-5-aminoquinoxaline was synthesized by the following methods (1) to (3).

(1) Synthesis of 2,3-diaminonitrobenzene

[0040]



[0041] 14 g of commercial 1-amino-2,5-dinitrobenzene was dissolved in 225 ml of methanol, and a solution of 60 g of sodium sulfate and 21 g of sodium hydrogencarbonate in 240 g was added to the methanol solution by use of a dropping funnel while maintaining the reaction temperature at 60°C. After the addition was over, the mixture was further stirred at 60°C for 1 hr. After the reaction was over, the reaction mixture was cooled to room temperature, and the crystal precipitated was filtered out.

Amount obtained: 7.79 g (Yield 66.5%)

Red brown microcrystals

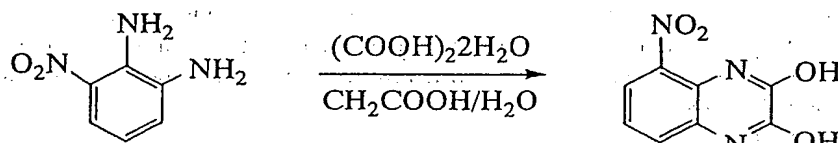
Melting point: 140°C

m/z: (FD+) 153 (Calcd.: 153.1396)

¹H-NMR(500 MHz, d₆-DMSO, δ ppm): 7.72, 7.70, 7.24, 6.92, 6.62, 6.61, 6.60, 6.59, 5.92, 3.40.

(2) Synthesis of 2,3-dihydroxy-5-nitroquinoxaline

[0042]



[0043] 4 g (26.12 mmol) of 2,3-diaminonitrobenzene and 6.59 g (52.24 mmol) of commercial oxalic acid were dissolved in 50% acetic acid, and reaction was allowed at boiling point under an argon stream for 3 hr. After the reaction was over, the reaction mixture was cooled to room temperature, and the crystal precipitated was filtered out.

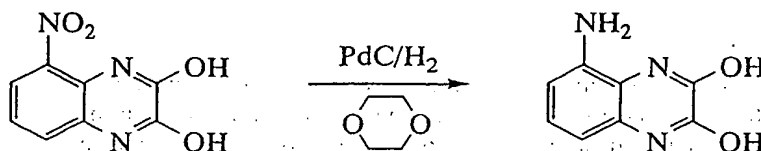
Amount obtained: 3.01 g (Yield: 55.6%)

Yellow microcrystals

m/z: 207 (Calcd.: 207.144)

(3) Synthesis of 2,3-dihydroxy-5-aminoquinoxaline

[0044]



[0045] 2.00 g of 2,3-dihydroxy-5-nitroquinoxaline was dissolved in 1:1 mixed solvent of methanol/dioxane, then the reaction system was sufficiently flushed with argon, and 1.00 g of Pd/C (anhydrous) was added to the reaction mixture. Thereafter, the reaction system was flushed with hydrogen, and reaction was allowed at room temperature for 20 hr.

After the reaction was over, the reaction mixture was dispersed in a solution of 6.00 g of potassium carbonate in 130 ml of water, thereby dissolving the reaction product. Filtration was conducted, and 35% hydrochloric acid was gradually added to the solution obtained upon the filtration, to obtain precipitates.

Amount obtained: 1.10 g

Pale yellow microcrystals

m/z(FD+): 177 (Calcd.: 177.1616)

^{13}C -NMR(500 MHz, d_6 -DMSO, δ ppm): 155.80, 155.65, 135.96, 126.84, 124.13, 112.33, 109.60, 103.84.

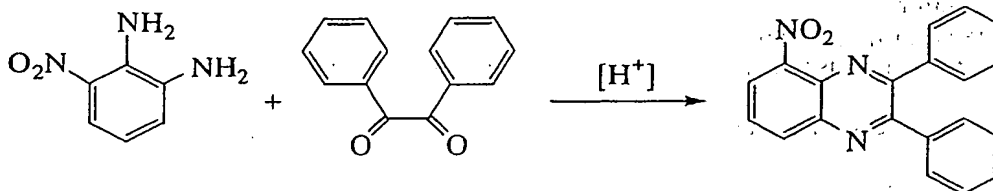
Synthesis Example 2

Synthesis of 2,3-Diphenyl-5-aminoquinoxaline

[0046] 2,3-Diphenyl-5-aminoquinoxaline was synthesized by the following methods (1) and (2).

(1) Synthesis of 2,3-diphenyl-5-nitroquinoxaline

[0047]



[0048] 1.53 g (10 mmol) of 2,3-diaminonitrobenzene and 2.00 g (9.6 mmol) of benzil were placed in a four-necked flask, and were dissolved by adding a 1:1 mixed solvent of acetic acid/methanol thereto. Thereafter, reaction was allowed at 70°C for 2 hr. After the reaction, the solvent was removed, and the reaction product was extracted on a silica gel column (ethyl acetate:hexane=1:1).

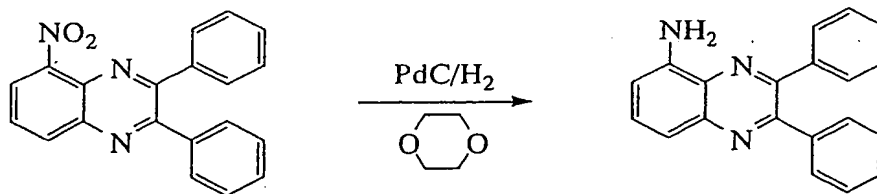
Amount obtained: 2.11 g

Yellow microcrystals

m/z(FD+): 327 (Calcd.: 327.24)

(2) Synthesis of 2,3-diphenyl-5-aminoquinoxaline

[0049]



[0050] 1.04 g of 2,3-diphenyl-5-nitroquinoxaline was dissolved in 30 g of dioxane, then the reaction system was flushed with argon, and 0.5 g of Pd/C (anhydrous) was added to the reaction mixture. After the reaction system was again flushed with argon sufficiently, hydrogen was added thereto, and reaction was allowed at room temperature for 30 hr. After the reaction was over, filtration was conducted, the reaction solvent was removed, and the reaction product was separated and purified on a silica gel column (ethyl acetate:hexane=1:3).

Amount obtained: 0.73 g

Yellow microcrystals

m/z: 297 (Calcd. M: 297.36)

^{13}C -NMR(500 MHz, CDCl_3 , δ ppm): 153.61, 150.12, 144.23, 141.96, 139.45, 139.35, 131.13, 130.09, 129.94, 128.77, 128.65, 128.35, 128.17, 117.21, 110.25.

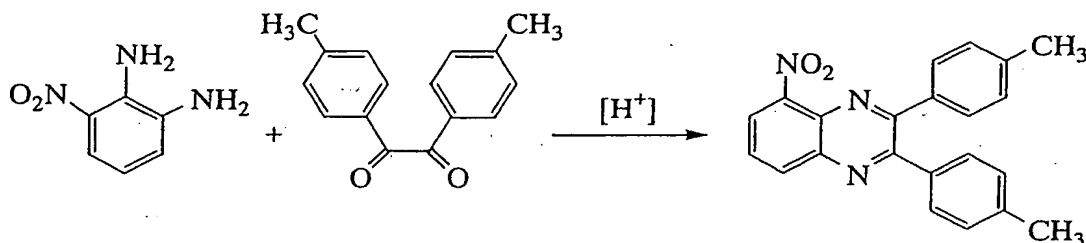
Synthesis Example 3

Synthesis of 2,3-Di(4-methylphenyl)-5-aminoquinoxaline

[0051] 2,3-Di(4-methylphenyl)-5-aminoquinoxaline was synthesized by the following methods (1) and (2).

(1) Synthesis of 2,3-di(4-methylphenyl)-5-nitroquinoxaline

[0052]



[0053] 1.84 g (12 mmol) of 2,3-diaminonitrobenzene and 2.38 g (10 mmol) of 4,4'-dimethylbenzil were dissolved in 40 g of a 1:1 mixed solvent of acetic acid/methanol, and reaction was allowed at 80°C for 4 hr. After the reaction was over, the solvent was removed, and the reaction product was extracted on a silica gel column.

Amount obtained: 1.30 g

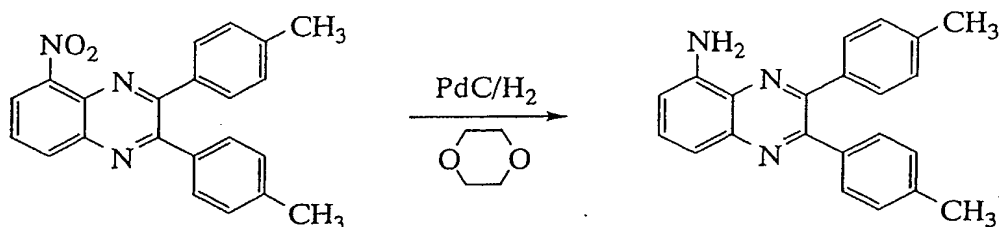
Yellow microcrystals

m/z: 355 (Calcd. M: 355.39)

^{13}C -NMR(500 MHz, CDCl_3 , δ ppm): 154.90, 154.83, 147.09, 140.76, 140.13, 139.86, 135.60, 135.13, 133.71, 133.23, 130.28, 129.70, 129.32, 129.12, 128.41, 127.75, 124.21.

(2) Synthesis of 2,3-di(4-methylphenyl)-5-aminoquinoxaline

[0054]



[0055] 2.02 g (0.0057 mol) of 2,3-di(4-methylphenyl)-5-nitroquinoxaline was dissolved in 30 g of dioxane, then the reaction system was flushed with argon, and 0.6 g of PdC (anhydrous) was added thereto. After the reaction system was again flushed with argon, it was flushed with hydrogen, and reaction was allowed at room temperature for 18 hr. After the reaction was over, the reaction mixture was filtered, the filter cake was washed with acetone and dioxane, and filtration was again conducted. The solvent was removed from the filtrate obtained, and the reaction product was extracted on a silica gel column.

Amount obtained: 1.36 g

Yellow microcrystals

m/z: 325 (Calcd.: 325.14)

^{13}C -NMR(500 MHz, CDCl_3 , δ ppm): 153.61, 150.16, 144.09, 141.86, 138.66, 138.59, 136.70, 136.67, 131.27, 130.78, 129.93, 129.78, 129.04, 128.98, 117.24, 110.06.

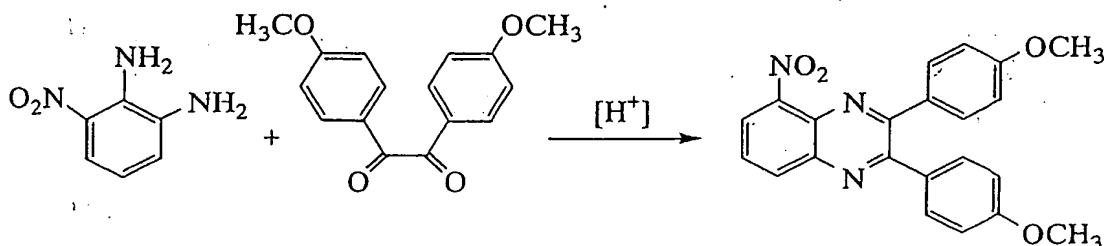
Synthesis Example 4

Synthesis of 2,3-di(4-methoxyphenyl)-5-aminoquinoxaline

[0056] 2,3-Di(4-methoxyphenyl)-5-aminoquinoxaline was synthesized by the following methods (1) and (2).

(1) Synthesis of 2,3-(4-dimethoxyphenyl)-nitroquinoxaline

[0057]



[0058] 1.54 g (10 mmol) of 2,3-aminonitrobenzene and 2.25 g (8.3 mmol) of 4,4'-dimethoxybenzil were dissolved in 100 g of a 1:1 mixed solvent of methanol/acetic acid, and reaction was allowed at room temperature for 20 hr. After the reaction was over, the reaction mixture was filtrated. The filter cake was further washed with acetone and dioxane, and filtration was again conducted. The solvent was removed from the filtrate obtained, and the reaction product was extracted on a silica gel column.

Amount obtained: 1.24 g

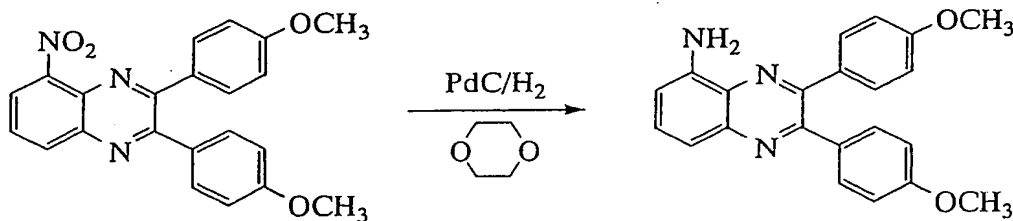
Yellow microcrystals

m/z: 387 (Calcd.: 387.39)

^{13}C -NMR(500 MHz, CDCl_3 , δ ppm): 161.10, 160.91, 154.33, 154.25, 146.95, 140.65, 133.60, 133.14, 131.92, 130.84, 130.41, 127.51, 124.10, 114.10, 113.88.

(2) Synthesis of 2,3-di(4-methoxyphenyl)-5-aminoquinoxaline

[0059]



[0060] 0.55 g (0.0014 mol) of 2,3-(4-dimethoxyphenyl)-5-nitroquinoxaline was dissolved in 30 g of dioxane, the reaction system was flushed sufficiently with argon, then 0.5 g of PdC was added thereto, and the reaction system was again flushed sufficiently with argon. The system was flushed with hydrogen gas, and reaction was allowed at room temperature for 24 hr. After the reaction was over, the reaction mixture was filtrated. The filter cake was further washed with acetone and dioxane, and filtration was again conducted. The solvent was removed from the filtrate obtained, and the reaction product was extracted on a silica gel column.

Amount obtained: 0.37 g

Yellow microcrystals

m/z: 325 (Calcd.: 325.43)

^{13}C -NMR(500 MHz, CDCl_3 , δ ppm): 160.14, 150.06, 153.13, 149.74, 144.01, 141.75, 131.39, 131.29, 130.62, 117.16, 113.83, 113.66, 110.01, 55.38.

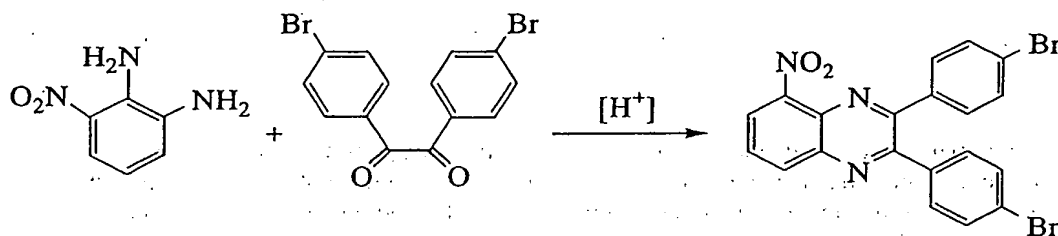
Synthesis Example 5

Synthesis of 2,3-di(4-bromophenyl)-5-aminoquinoxaline

[0061] 2,3-di(4-bromophenyl)-5-aminoquinoxaline was synthesized by the following methods (1) and (2).

(1) Synthesis of 2,3-di(4-bromophenyl)-5-nitroquinoxaline

[0062]



[0063] 1.53 g (10 mmol) of 2,3-diaminonitrobenzene and 3.68 g (10 mmol) of 4,4'-dibromobenzil were dissolved in 80 g of a 1:1 mixed solvent of acetic acid/methanol, and reaction was allowed at 70°C for 30 hr. After the reaction was over, the solvent was removed, and the reaction product was extracted on a silica gel column.

Amount obtained: 1.89 g

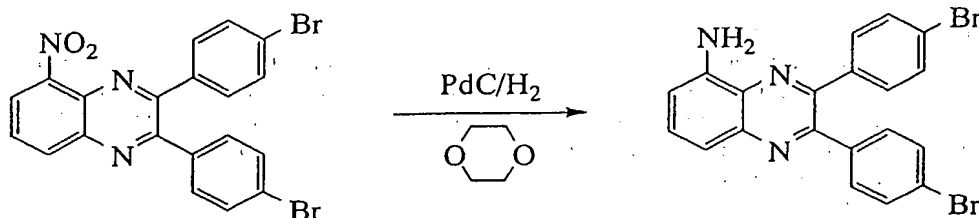
Yellow microcrystals

m/z: 485 (Calcd.: 485.12)

^{13}C -NMR(500 MHz, CDCl_3 , δ ppm): 153.45, 153.36, 147.01, 140.79, 136.81, 136.38, 133.78, 133.26, 132.05, 131.87, 131.82, 131.38, 128.58, 124.98, 124.88, 124.71.

(2) Synthesis of 2,3-di(4-bromophenyl)-5-aminoquinoxaline

[0064]



[0065] 1.01 g (0.0021 mol) of 2,3-di(4-bromophenyl)-5-nitroquinoxaline was dissolved in 30 g of dioxane, and the reaction system was flushed sufficiently with argon. Thereafter, 0.3 g of PdC was added to the reaction mixture, the reaction system was again flushed sufficiently with argon, the system was then flushed with hydrogen gas, and reaction was allowed at room temperature for 24 hr. After the reaction was over, the reaction mixture was filtered, the filter cake was further washed with acetone and dioxane, and filtration was again conducted. The solvent was removed from the filtrate obtained, and the reaction product was extracted on a silica gel column.

Amount obtained: 0.66 g

Yellow microcrystals

m/z: 455 (Calcd.: 455.12)

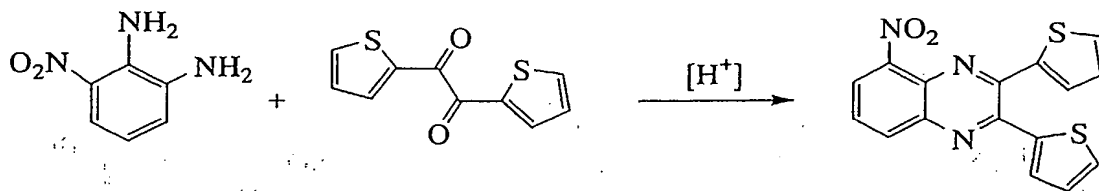
Synthesis Example 6

5 Synthesis of 2,3-Dithienyl-5-aminoquinoxaline

[0066] 2,3-Dithienyl-5-aminoquinoxaline was synthesized by the following methods (1) and (2).

10 (1) Synthesis of 2,3-dithienyl-5-nitroquinoxaline

[0067]



[0068] 0.022 g (0.099 mmol) of 2,3-diaminonitrobenzene and 0.01938 g (0.198 mmol) of 2,2'-thienyl were dissolved in 3 g of a 1:1 mixed solvent of acetic acid/methanol, and reaction was allowed at 70°C for 30 hr. After the reaction was over, the solvent was removed, and the reaction product was extracted on a silica gel column.

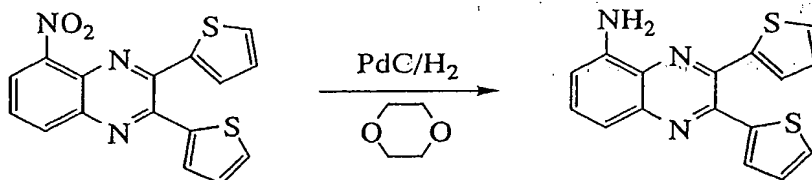
Amount obtained: 0.04 g

Yellow microcrystals

m/z: 339 (Calcd.: 339.40)

30 (2) Synthesis of 2,3-dithienyl-5-aminoquinoxaline

[0069]



[0070] 1.01 g (0.0030 mol) of 2,3-dithienyl-5-nitroquinoxaline was dissolved in 30 g of dioxane, and the reaction system was flushed sufficiently with argon. Thereafter, 0.3 g of PdC was added to the reaction mixture, the reaction system was again flushed sufficiently with argon, the system was then flushed with hydrogen gas, and reaction was allowed at room temperature for 24 hr. After the reaction was over, the reaction mixture was filtered, the filter cake was further washed with acetone and dioxane, and filtration was again conducted. The solvent was removed from the filtrate obtained, and the reaction product was extracted on a silica gel column.

Amount obtained: 0.40 g

Yellowish brown microcrystals

m/z: 309 (Calcd.: 309.42)

Example 1

55 Synthesis of Poly(2,3-diphenyl-5-aminoquinoxaline)

[0071] 1.1698 g of hydrochloric acid was added to 0.1490 g of 2,3-diphenyl-5-aminoquinoxaline obtained in Synthesis Example 2, whereby 2,3-diphenyl-5-aminoquinoxaline was dissolved as a hydrochloride. Thereafter, 6.0 g of DMF solvent was added to the solution.

[0072] Electrolytic polymerization was conducted by using Ag/Ag⁺ as a reference electrode, a platinum mesh electrode as a counter electrode, and ITO as a working electrode. The electrolytic polymerization was conducted potentiostatically at a potential of 1300 mV for 1000 sec. The solid obtained was analyzed by TOF (time of flight) mass spectrometry, and was identified.

Example 2

Synthesis of Poly(2,3-di(4-methylphenyl)-5-aminoquinoxaline)

[0073] 0.16 g of 2,3-di(4-methylphenyl)-5-aminoquinoxaline obtained in Synthesis Example 3 was dissolved in 0.54 g of hydrochloric acid, and 6.5 g of DMF was added to the solution. Electrolytic polymerization was conducted by using Ag/Ag⁺ as a reference electrode, a platinum mesh electrode as a counter electrode, and ITO as a working electrode. The electrolytic polymerization was conducted potentiostatically at a potential of 1300 mV for 1000 sec. The solid obtained was analyzed by TOF mass spectrometry, and was identified.

Example 3

Synthesis of Poly(2,3-di(4-dimethoxyphenyl)-5-aminoquinoxaline)

[0074] 0.17 g of 2,3-di(4-dimethoxyphenyl)-5-aminoquinoxaline obtained in Synthesis Example 4 was dissolved in 1.12 g of hydrochloric acid, and 6.5 g of DMF was added to the solution. Electrolytic polymerization was conducted by using Ag/Ag⁺ as a reference electrode, a platinum mesh electrode as a counter electrode, and ITO as a working electrode. The electrolytic polymerization was conducted potentiostatically at a potential of 1300 mV for 1000 sec. The solid obtained was analyzed by TOF mass spectrometry, and was identified.

Example 4

Synthesis of Poly(2,3-di(4-bromophenyl)-5-aminoquinoxaline)

[0075] 0.45 g of 2,3-di(4-bromophenyl)-5-aminoquinoxaline obtained in Synthesis Example 5 was dissolved in 1.12 g of hydrochloric acid, and 6.5 g of DMF was added to the solution. Electrolytic polymerization was conducted by using Ag/Ag⁺ as a reference electrode, a platinum mesh electrode as a counter electrode, and ITO as a working electrode. The electrolytic polymerization was conducted potentiostatically at a potential of 1300 mV for 1000 sec. The solid obtained was analyzed by TOF mass spectrometry, and was identified.

Example 5

Synthesis of Poly(2,3-dithienyl-5-aminoquinoxaline)

[0076] 0.36 g of 2,3-dithienyl-5-aminoquinoxaline obtained in Synthesis Example 6 was dissolved in 1.12 g of hydrochloric acid, and 6.5 g of DMF was added to the solution. Electrolytic polymerization was conducted by using Ag/Ag⁺ as a reference electrode, a platinum mesh electrode as a counter electrode, and ITO as a working electrode. The electrolytic polymerization was conducted potentiostatically at a potential of 1300 mV for 1000 sec. The solid obtained was analyzed by TOF mass spectrometry, and was identified.

Example 6

Chemical Oxidation Polymerization of Poly(2,3-diphenyl-5-aminoquinoxaline)

[0077] 0.24 g (0.80 mmol) of 2,3-diphenyl-5-aminoquinoxaline obtained in Synthesis Example 2 was dissolved in 17 ml of 35% hydrochloric acid, and 12 g of DMF was added to the solution. To the resulting solution, an aqueous solution of 0.18 g (0.80 mmol) of ammonium persulfate in 2 g of water was added dropwise at a reaction temperature of 10°C. After the dropwise addition, the reaction mixture was stirred at room temperature for 24 hours, to effect reaction. After the reaction was over, the reaction product was filtered out, then washed with methanol and acetone, and the remaining solid matter was analyzed by TOF mass spectrometry, and was identified.

Example 7

Chemical Oxidation Polymerization of Poly(2,3-di(4-methylphenyl)-5-aminoquinoxaline)

[0078] 0.268 g (0.80 mmol) of 2,3-di(4-methylphenyl)-5-aminoquinoxaline obtained in Synthesis Example 3 was dissolved in 17 ml of 35% hydrochloric acid, and 12 g of DMF was added to the solution. To the resulting solution, an aqueous solution of 0.18 g (0.80 mmol) of ammonium persulfate in 2 g of water was added dropwise at a reaction temperature of 10°C. After the dropwise addition, the reaction mixture was stirred at room temperature for 24 hr, to effect reaction. After the reaction was over, the reaction product was filtered out, then washed with methanol and acetone, and the remaining solid matter was analyzed by TOF mass spectrometry, and was identified.

Example 8

Chemical Oxidation Polymerization of Poly(2,3-di(4-methoxyphenyl)-5-aminoquinoxaline)

[0079] 0.29 g (0.80 mmol) of 2,3-di(4-methoxyphenyl)-5-aminoquinoxaline obtained in Synthesis Example 4 was dissolved in 17 ml of 35% hydrochloric acid, and 12 g of DMF was added to the solution. To the resulting solution, an aqueous solution of 0.18 g (0.80 mmol) of ammonium persulfate in 2 g of water was added dropwise at a reaction temperature of 10°C. After the dropwise addition, the reaction mixture was stirred at room temperature for 24 hr, to effect reaction. After the reaction was over, the reaction product was filtered out, then washed with methanol and acetone, and the remaining solid matter was analyzed by TOF mass spectrometry, and was identified.

[Molecular Weight and Molecular Weight Distribution of Polymers]

[0080] The poly(5-aminoquinoxalines) of the general formula (1) obtained in Examples 1 to 5 above were subjected to molecular weight measurement by TOF mass spectrometry. The results are shown in Table 1 below.

Table 1

Molecular Weight Determined by TOF Mass Spectrometry				
Example	Polymer	Mn	Mw	Mz
Example 1	Poly(2,3-diphenyl-5-aminoquinoxaline)	1230	1923	1656
Example 2	Poly(2,3-di(4-methylphenyl)-5-aminoquinoxaline)	1194	1850	1628
Example 3	Poly(2,3-di(4-dimethoxyphenyl)-5-aminoquinoxaline)	4547	3500	3012
Example 4	Poly(2,3-di(4-bromophenyl)-5-aminoquinoxaline)	2123	2851	2492
Example 5	Poly(2,3-dithienyl-5-aminoquinoxaline)	1353	1557	1463
Example 6	Poly(2,3-diphenyl-5-aminoquinoxaline)	1039	1054	
Example 7	Poly(2,3-di(4-methylphenyl)-5-aminoquinoxaline)	1154	1197	
Example 8	Poly(2,3-di(4-methoxyphenyl)-5-aminoquinoxaline)	1354	1278	
Mn: number average molecular weight Mw: weight average molecular weight Mz: z average molecular weight				

Example 9

Chemical Oxidation Polymerization of Poly(2,3-diphenyl)-5-aminoquinoxaline

[0081] 0.24 g (0.80 mmol) of 2,3-diphenyl-5-aminoquinoxaline obtained in Synthesis Example 2 was dissolved in 1 g of chloroform. To the resulting solution, 1 g of chloroform having 0.001 g of anhydrous ferric chloride (FeCl_3) dissolved therein was added dropwise at room temperature under nitrogen gas atmosphere. After the dropwise addition, the reaction mixture was stirred at room temperature for 24 hours, to effect polymerization reaction.

Example 10

Chemical Oxidation Polymerization of Poly(2,3-diphenyl)-5-aminoquinoxaline

[0082] 0.24 g (0.80 mmol) of 2,3-diphenyl-5-aminoquinoxaline obtained in Synthesis Example 2 was dissolved in 1 g of chloroform. To the resulting solution, 1 g of chloroform having 0.001 g of anhydrous ferric chloride (FeCl_3) dissolved therein was added dropwise at room temperature under nitrogen gas atmosphere. After the dropwise addition, the reaction mixture was stirred at a temperature of 40°C for 24 hours, to effect polymerization reaction.

Example 11

Chemical Oxidation Polymerization of Poly(2,3-diphenyl)-5-aminoquinoxaline

[0083] 0.24 g (0.80 mmol) of 2,3-diphenyl-5-aminoquinoxaline obtained in Synthesis Example 2 was dissolved in 1 g of chloroform. To the resulting solution, 1 g of chloroform having 0.001 g of anhydrous ferric chloride (FeCl_3) dissolved therein was added dropwise at room temperature under nitrogen gas atmosphere. After the dropwise addition, the reaction mixture was stirred at a temperature of 60°C for 24 hours, to effect polymerization reaction.

Example 12

Chemical Oxidation Polymerization of Poly(2,3-di(4-methylphenyl)-5-aminoquinoxaline)

[0084] 0.26 g (0.80 mmol) of 2,3-di(4-methylphenyl)-5-aminoquinoxaline obtained in Synthesis Example 3 was dissolved in 1 g of chloroform. To the resulting solution, 1 g of chloroform having 0.001 g of anhydrous ferric chloride (FeCl_3) dissolved therein was added dropwise at room temperature under nitrogen gas atmosphere. After the dropwise addition, the reaction mixture was stirred at room temperature for 24 hours, to effect polymerization reaction.

Example 13

Chemical Oxidation Polymerization of Poly(2,3-di(4-methylphenyl)-5-aminoquinoxaline)

[0085] 0.26 g (0.80 mmol) of 2,3-di(4-methylphenyl)-5-aminoquinoxaline obtained in Synthesis Example 2 was dissolved in 1 g of chloroform. To the resulting solution, 1 g of chloroform having 0.001 g of anhydrous ferric chloride (FeCl_3) dissolved therein was added dropwise at room temperature under nitrogen gas atmosphere. After the dropwise addition, the reaction mixture was stirred at a temperature of 60°C for 24 hours, to effect polymerization reaction.

[0086] After the reaction (each reaction of Examples 9-13) was over, the reaction product was filtered out, and then purified by reprecipitation with methanol. The molecular weight of the resulting polymer was measured by GPC in the following measurement condition.

Column: TSK Gel super H3000 (TOSOH CORPORATION)

Eluent: DMF (0.6 ml/min; 3.5 MPa)

Table 2

Molecular Weight by GPC			
Example	Polymer	Mn	Mw
Example 9	Poly(2,3-diphenyl-5-aminoquinoxaline)	54600	63200
Example 10	Poly(2,3-diphenyl-5-aminoquinoxaline)	78400	83500
Example 11	Poly(2,3-diphenyl-5-aminoquinoxaline)	63200	65400
Example 12	Poly(2,3-di(4-methylphenyl)-5-aminoquinoxaline)	38500	43400
Example 13	Poly(2,3-di(4-methylphenyl)-5-aminoquinoxaline)	54300	55400
Mn: number average molecular weight			
Mw: weight average molecular weight			

[Measurement of Electrical Conductivity]

[0087] The poly(aminoquinoxalines) of the general formula (1) obtained in Examples 1 to 5 above were subjected to measurement of electrical conductivity as follows. Each polymer was favorably molded into a pellet by a compression molding machine, the pellet was cut to a rectangular shape, the rectangular specimen was fixed between two platinum electrodes by use of a carbon paste, and the electrical conductivity of the specimen was measured (two terminal method).

[0088] As a result, it was found that the polymers appear to be yellow to red in color in the state of being doped with hydrochloric acid. The results of measurement of electrical conductivity are shown in Table 2 below.

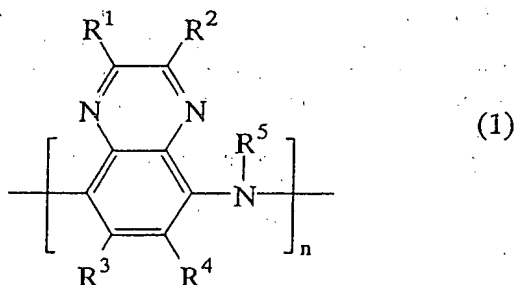
Table 3

Example	Polymer	Conductivity (S/cm)
Example 1	Poly(2,3-diphenyl-5-aminoquinoxaline)	100
Example 2	Poly(2,3-di(4-methylphenyl)-5-aminoquinoxaline)	100
Example 3	Poly(2,3-di(4-dimethoxyphenyl)-5-aminoquinoxaline)	70
Example 4	Poly(2,3-di(4-bromophenyl)-5-aminoquinoxaline)	80
Example 5	Poly(2,3-dithienyl-5-aminoquinoxaline)	70

[0089] The present invention is not limited to the details of the above described preferred embodiments. The scope of the invention is defined by the appended claims and all changes and modifications as fall within the equivalence of the scope of the claims are therefore to be embraced by the invention.

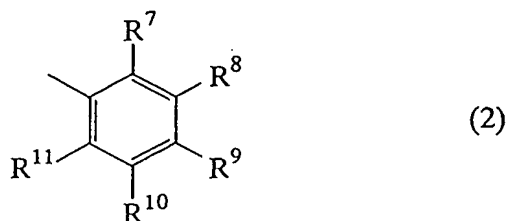
Claims

1. A poly(5-aminoquinoxaline) having the general formula (1):



in which R¹ and R² each independently represent a hydrogen atom, a hydroxyl group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a thienyl group, a substituted thienyl group, a naphthyl group, a substituted naphthyl group, a pyrrolyl group, a substituted pyrrolyl group, a furyl group, a substituted furyl group, an alkyl group, or an alkoxy group; R³ and R⁴ each independently represent a hydrogen atom, an alkyl group, an alkoxy group, a cyano group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a thienyl group, a substituted thienyl group, a pyrrolyl group, a substituted pyrrolyl group, a furyl group, a substituted furyl group, a naphthyl group, or a substituted naphthyl group; R⁵ represents a hydrogen atom, an alkyl group, an alkoxy group, an acetyl group, a cyano group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a thienyl group, a substituted thienyl group, a pyrrolyl group, a substituted pyrrolyl group, a naphthyl group, or a substituted naphthyl group; and n represents a positive integer of not less than three.

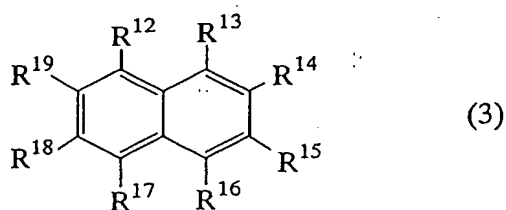
2. A poly(5-aminoquinoxaline) as set forth in claim 1, wherein R¹ and R² in the general formula (1) comprise groups having the general formula (2):



in which R⁷ to R¹¹ each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, a cyanoalkyl group having one to four carbon atoms, a haloalkyl group having one to four carbon atoms, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group.

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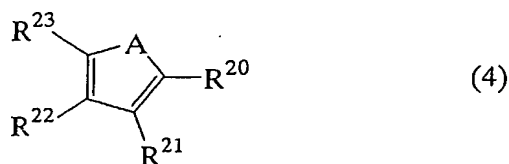
3. A poly(5-aminoquinoxaline) as set forth in claim 1, wherein R¹ and R² in the general formula (1) comprise groups having the general formula (3):
- 20



in which any one of R¹² to R¹⁹ is coupled to the quinoxaline ring, and the others of R¹² to R¹⁹ each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group.

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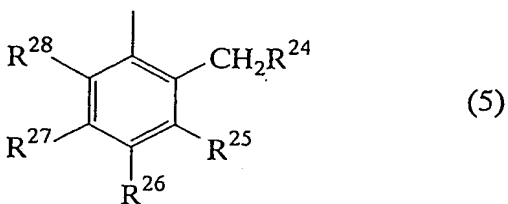
4. A poly(5-aminoquinoxaline) as set forth in claim 1, wherein R¹ and R² in the general formula (1) comprise groups having the general formula (4):
- 40



in which any one of R²⁰ to R²³ is coupled to the quinoxaline ring, and the others of R²⁰ to R²³ each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a biphenyl group, a substituted biphenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group; and A represents NH, O, or S.

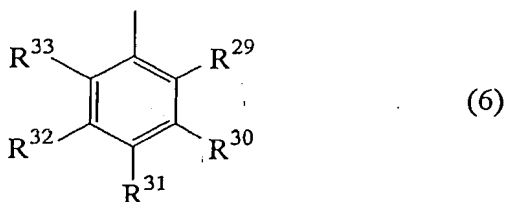
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5. A poly(5-aminoquinoxaline) as set forth in claim 1, wherein R¹ and R² in the general formula (1) comprise groups having the general formula (5):



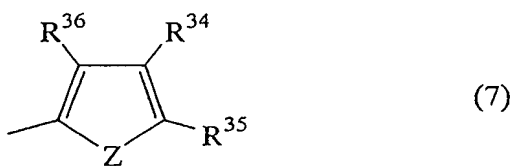
10 in which R²⁴ represents a halogen atom or a cyano group; and R²⁵ to R²⁸ each independently represent a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group.

- 15 6. A poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 5 wherein R⁵ in the general formula (1) is a group having the general formula (6):



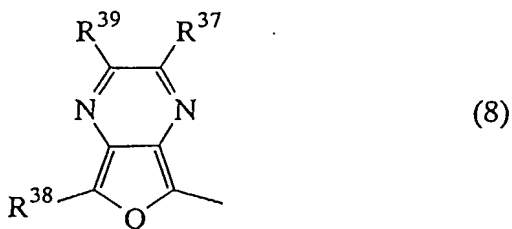
30 in which R²⁹ to R³³ each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group.

- 35 7. A poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 5 wherein R⁵ in the general formula (1) is a group having the general formula (7):



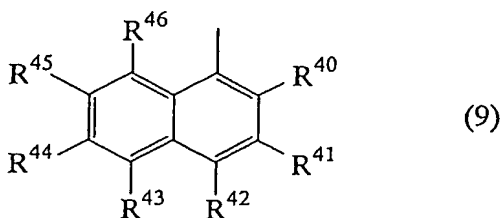
50 in which R³⁴ to R³⁶ each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group; and Z represents NH, O, or S.

- 55 8. A poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 5 wherein R⁵ in the general formula (1) is a group having the general formula (8):



15 in which R³⁷ to R³⁹ each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group; and Q represents NH, O, or S.

- 20 9. A poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 5 wherein R⁵ in the general formula (1) is a group having the general formula (9):



35 in which R⁴⁰ to R⁴⁶ each independently represent a hydrogen atom, a halogen atom, a cyano group, an amino group, an alkyl group having one to ten carbon atoms, an alkoxy group having one to ten carbon atoms, a nitro group, a phenyl group, a substituted phenyl group, a naphthyl group, a substituted naphthyl group, a thienyl group, a substituted thienyl group, an epoxy group, or a vinyl group.

- 40 10. A film formed by spin coating or casting of a poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 9.
11. A film formed by compression molding of a poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 9.
- 45 12. An electrochromic device comprised of a poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 9.
13. An active substance or an electrode for a battery, comprised of a poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 9.
- 50 14. A semiconductor comprised of a poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 9.
15. A p-type semiconductor produced by oxidizing a poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 9 by an oxidant or electrochemical doping.
- 55 16. An n-type semiconductor produced by reducing a poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 9 by a reducing agent or electrochemical doping.
17. A solar cell comprising a p-type semiconductor as set forth in claim 15 and an n-type semiconductor as set forth in claim 16.
18. An organic electroluminescence device comprised of a poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 9.

19. A non-linear organic material comprised of a poly(5-aminoquinoxaline) as set forth in any one of claims 1 to 9.

20. A process of preparation of a poly(5-aminoquinoxaline) according to any one of claims 1 to 9, comprising polymerising a corresponding 5-aminoquinoxaline.

21. A process of making an article comprising forming a poly(5-aminoquinoxaline) according to any one of claims 1 to 9.

22. A process according to claim 21 in which the article is according to any one of claims 10 to 19.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 03 25 2925

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	J. HRDLICKA, P. MATEJKA, ET AL.: "Comparison of FT Raman spectra of some 5-nitroquinoxalines and their electropolymers" JOURNAL OF MOLECULAR STRUCTURE, vol. 565-566, 30 May 2001 (2001-05-30), pages 101-105, XP002253994 * page 101, paragraph 1 * * page 103, paragraph 1 * * figure 1 *	1-13, 20-22	C08G73/06 H01L21/34
D,A	H. B. GILLESPIE, M. ENGELMAN, F. SPANO, S. GRAFF: "Some New o-Phenylenediamines and the Related Benzimidazoles, Benzotriazoles and Quinoxalines" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 79, no. 9, 5 May 1957 (1957-05-05), pages 2245-2248, XP002253995 * page 2246, column 1, paragraph 4 - column 2, paragraph 1 * * page 2248, column 1, paragraph 4 - paragraph 7 *	1-9	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C08G H01L
D,A	US 4 356 429 A (TANG CHING W) 26 October 1982 (1982-10-26) * claims * * figure 1 *	14-19	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 10 September 2003	Examiner Öhm, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP. 03 25 2925

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10-09-2003

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